

Microscopy of Clathrate Compounds: Determining the Structure and Hydrogen Encapsulating Properties through Aberration-Corrected HAADF-STEM.

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In the quest for alternative energy sources, hydrogen has long been touted as one of the most likely candidates to replace fossil fuels, provided practical solutions for its storage and transport can be found. Amongst other nano-porous materials such as zeolites, clathrate hydrates have shown remarkable potential for hydrogen storage, adsorbing up to 7.5%wt hydrogen, albeit in extreme pressure and temperature conditions [1]. Upon crystallising, these compounds form a three-dimensional host matrix where guest atoms can be accommodated within distinct polyhedral “cages”. Unlike their hydrate counterparts, however, silicon and germanium based inorganic clathrates had until now mostly been studied for their superconductivity and thermoelectric behaviour. The present work nevertheless exhibits two metal silicide clathrates, stable at room temperature, with promising hydrogen encapsulation properties [3].

The type-I silicon clathrate consists of a silicon matrix with two distinct guest sites, labelled *2a* and *6d*, occupied most commonly by alkali or alkali earth metal atoms. Magic angle spinning nuclear magnetic resonance has confirmed that, in the case of Na guest atoms and in the growth conditions specific to this work, the guest sites are Na deficient and H rich. The precise structure and stoichiometry of the resulting compound was subsequently investigated by aberration-corrected Z-contrast imaging on a 100kV VG HB501 dedicated scanning transmission electron microscope (STEM). When observed in (001) projection, the *6d* guest site, at the centre of the larger of the two polyhedral cages, is nicely isolated from neighbouring atoms. This allows the unequivocal determination of its occupancy through quantitative comparison with simulated images: figure 1. In the case of Na_xSi₄₆, it emerged that a third of the *6d* sites were Na-deficient and thus H-rich, yielding a stoichiometry consistent with the energy-dispersive X-ray (EDX) analysis of the compound. A similar investigation of the K_xSi₄₆ type-I clathrate revealed that in the case of potassium guests only a fifth of the large *6d* cages were K-deficient, whilst some of the smaller *2a* sites had to be deficient as well to explain the EDX results [3]. Rotating the structure into higher index zone axes, such as (111), see figure 2, and (110) to project the *2a* sites into different positions indeed confirmed these earlier findings. Due to the high precision needed for the analysis, great care was taken to decouple thickness effects and the contribution from neighbouring columns from the *2a* site contrast in the images. This general methodology on Na- and K-based type I clathrates is currently being extended to other structures: type III clathrates, and Ge/Ga-based compounds. The large unit cell of those compounds and their remarkable stability under the beam, as observed during experiments carried out at 300 kV whilst testing the new TEAM 0.5 microscope, make them ideal for this sort of pseudo three dimensional structure determination [4-5].

References

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- [4] Dr. B. Freitag's expertise must be gratefully acknowledged for the images obtained on the TEAM 0.5 microscope during testing at the FEI factory, Eindhoven.
- [5] The TEAM project is supported by the Department of Energy, Office of Science, Basic Energy Sciences. <http://ncem.lbl.gov/TEAM-project/>
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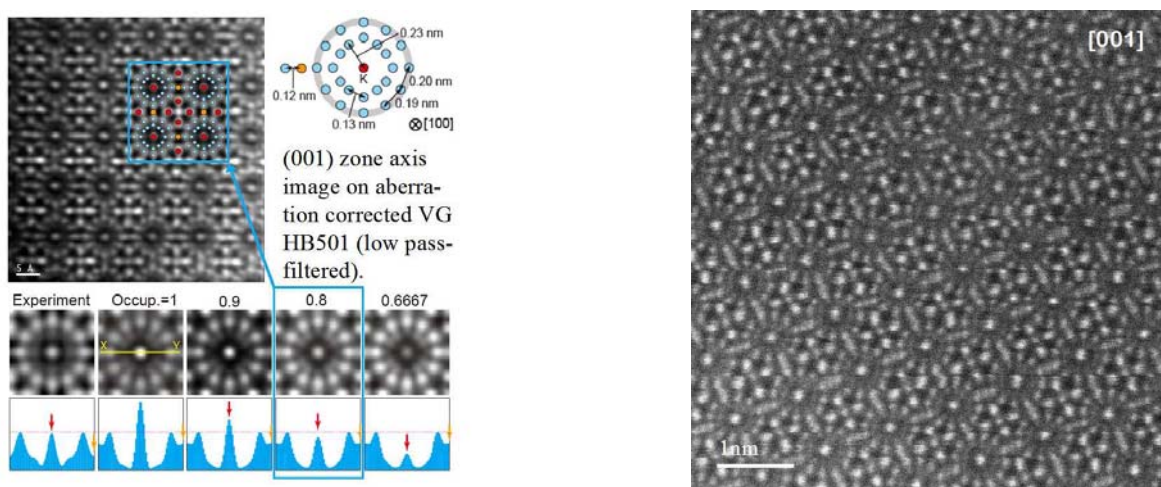


Figure 1. Determining the $6d$ site occupancy (coloured in red) through comparisons with image simulations. Left: image taken on an aberration-corrected VG HB501 (low pass filtered for clarity); right: unprocessed image of a neighbouring region, obtained at 300kV on the TEAM 0.5 microscope, showing the stability of the structure.

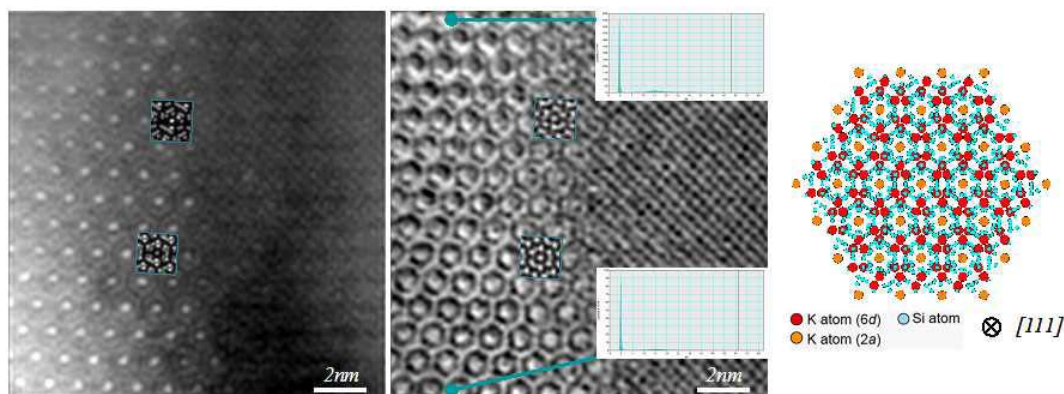


Figure 2. Tilting the grain to a (111) zone axis improves the line of sight to the $2a$ sites (coloured in orange). Insets are least-squares best fits to image simulations with an occupancy of 0.58. Also shown is the bright field image and low-loss spectra used to monitor sample thickness and increase the accuracy of the fit.